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(54)[TITLE]

Photoresist composition

(57)[Summary]

[OBJECT]

Development of the photoresist composition which is excellent in a photoresist useful as an adhesive agent and a coating agent, and an adhesive property.

[SUMMARY OF THE INVENTION]

It has the epoxy compound (A) containing a bisphenol A type epoxy resin, a cationic light polymerisation initiator (B), and an alkoxy silyl group.

An amino group contains alkoxy silyl the compound (C) which it does not have. That content becomes as follows to epoxy-compound (A) 100 weight parts. A cationic photopolymerization initiator (B) is 0.1 - 10 weight parts. The photoresist composition alkoxy silyl whose compound (C) is 0.1 - 10 weight parts.

[CLAIMS]

[CLAIM 1]

A photoresist composition, which has an epoxy compound (A), a cationic photopolymerization initiator (B), and an alkoxy silyl group.

An amino group contains alkoxy silyl the compound (C) which it does not have. That content becomes as follows to epoxy-compound (A) 100 weight parts. A cationic photopolymerization initiator is 0.1 - 10 weight parts. Alkoxy silyl a compound (C) is 0.1 - 10 weight parts.

[CLAIM 2]

A photoresist composition described in Claim 1 which is that in which an above-mentioned epoxy compound (A) includes the bisphenol A type epoxy resin more than that amount of 1/2.

[CLAIM 3]

A photoresist composition described in Claims 1 or 2 whose above-mentioned cationic photopolymerization initiators (B) are an aromatic sulfonium salt.

[DETAILED DESCRIPTION OF INVENTION]**[0001]****[INDUSTRIAL APPLICATION]**

This invention relates to the photoresist composition which hardens quickly by optical irradiation.

Especially the photoresist composition of this invention is utilised for an adhesive agent, a coating agent, etc.

[0002]**[PRIOR ART]**

In recent years, various photoresist composition and various photoresist come to attention.

Moreover, the method of hardening resin by irradiation of a light is applied in the various field.

When giving an example, there is epoxy (meth)acrylate resin currently disclosed by the resin composition which contains the urethane (meth)acrylate and the acrylate monomer which are disclosed by the unexamined-Japanese-patent-No. 57-172915 gazette, and the unexamined-Japanese-patent-No. 62-333651 gazette.

Moreover, it is also known that various epoxy resin hardens by cationic light polymerisation initiators, such as an aromatic diazonium salt, an aromatic iodonium salt, and an aromatic sulfonium salt.

[0003]

The hardening method by irradiation of a light becomes as follows compared with the heating hardening method. (1) The cure time is short.

(2) The hardening in low temperature is possible. (3) Do not need a solvent, or in small amount, since it is sufficient, it is saving resources.

And the environmental pollution is few. It has the advantage of these etc.

[0004]**[PROBLEM ADDRESSED]**

This invention is formed in consideration of the above-mentioned realisation.

It aims at an offer of the photoresist composition which is excellent in a photoresist useful as an adhesive agent and a coating agent, and an adhesive property.

[0005]**[SOLUTION OF THE INVENTION]**

These inventors have inquired about the photoresist composition useful as an adhesive agent and a coating agent.

When that process examines a well-known photoresist composition and a well-known photoresist, the composition which essentially consists of resin which performs a hardening (polymerisation) is excellent in an adhesive property with a cationic light polymerisation initiator.

And it has the characteristic of not receiving the hardening inhibition by oxygen. It became clear that it is useful as an adhesive agent and a coating agent.

[0006]

This invention is invention formed as a result of such a study.

That is, it has an epoxy compound (A), a cationic light polymerisation initiator (B), and an alkoxy silyl group.

An amino group contains alkoxy silyl the compound (C) which it does not have.

That content becomes as follows to epoxy-compound (A) 100 weight parts. A cationic photopolymerization initiator is 0.1 to 10 weight parts. Alkoxy silyl-compound (C) is 0.1 - 10 weight parts.

The photoresist composition which is characterised by the above-mentioned is offered.

[0007]

Below, this invention is explained in detail.

First, the component of this invention is explained.

[0008]

The epoxy compound (A) used with this invention is a compound which has the epoxy group of the at least one in that molecule.

If it has an epoxy group in a molecule, especially the structure of other parts will not be limited.

However, it is as follows when giving an example.

[0009]

Namely, bisphenol A, the bisphenol F, etc. the bisphenol A type epoxy resin

which an epichlorohydrin is made to react and is obtained, a bisphenol F-type epoxy resin, etc. the epoxy resin which hydrogenated to these, a cycloaliphatic epoxy resin, a glycidyl ester type epoxy resin, a novolak type epoxy resin, the urethane denaturation epoxy resin which has a urethane bond, the nitrogen-containing epoxy resin which performed the epoxidated of a meta-xylene diamine, the hydantoin, etc., they are various epoxy resins, such as the rubber denaturation epoxy resin which contains a polybutadiene or NBR, the various mono epoxide compound referred to a reactant thinner, a di epoxide compound, a tri epoxide compound, etc.

[0010]

It is desirable to use a bisphenol A type epoxy resin as an epoxy compound (A) with this invention.

[0011]

A bisphenol A type epoxy resin means bisphenol A, the compound shown by the following general formula (I) synthesised from an epichlorohydrine, and the compound shown by the following general formula (II) synthesised from bisphenol A and (beta)-methyl epichlorohydrine.

[0012]**[COMPOUND 1]**

(Where, n is 0 or a positive integer)

[0013]**[COMPOUND 2]**

(Where, n is 0 or a positive integer)

[0014]

Specifically, Epiklon 850S (product made from the Dainippon Ink chemistry Co., Ltd.), Sumiepoxy ESA011 (made in Sumitomo Chemical), Epicoat 828 (product made from Yuka Shell epoxy Co., Ltd.), KRM-2410 (made in Asahi Denka Kogyo), etc. are mentioned. However, many varieties are known.

[0015]

As the one part or all of epoxy compounds (A), when using a bisphenol A type

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epoxy resin, the photoresist composition of this invention becomes as follows.
That curing substance is excellent in an adhesive property.
Where, a cure rate goes in the direction to become small.
In addition, it is desirable to make into a bisphenol A type epoxy resin more than the amount of 1/2 of an epoxy compound (A) from that adhesive viewpoint.

[0016]

Moreover, it is desirable to use a cycloaliphatic epoxy resin as an epoxy compound (A) with this invention.

[0017]

With a cycloaliphatic epoxy resin, it has an alicyclic group in that molecule.
And, a part of alicyclic group is the compound by which the epoxidation is performed.
That is, it is the compound which has a cyclohexene oxide group, a tricyclo decene oxide group, a cyclopentene oxide group, etc.
Specifically, vinyl cyclohexene di epoxide (KRM-2206, made in Asahi Denka Kogyo), Vinyl cyclohexene mono epoxide, 3, 4-epoxy cyclohexyl methyl -3, 4-epoxy cyclohexane carboxylate (ERL-4221, made in a union calcium-carbide company), 2-(3, 4-epoxy cyclohexyl -5, 5-spiro -3, 4-epoxy) cyclohexane-m-dioxane (ERL-4234, made in a union calcium-carbide company), A bis- (3, 4-epoxy cyclohexyl) adipate (ERL-4299, made in a union calcium-carbide company) etc. is mentioned.

[0018]

The cure rate of cycloaliphatic epoxy resin is large.

[0019]

The cationic photopolymerization initiator (B) used with this invention means cationic compounds, such as an aromatic diazonium salt, an aromatic iodonium salt, an aromatic sulfonium salt, and an aromatic selenium salt.
Each dissolves these cationic photopolymerization initiators (B) by the ultraviolet, the electron beam, etc.
The discharge of the Lewis' acid is performed.
This Lewis' acid polymerises an epoxy group.

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[0020]

When describing a cationic light polymerisation initiator (B) more concretely, that cation part is structure shown by following formulas a-o.

Corresponding anion parts are SbF_6^- , AsF_6^- , PF_6^- , BF_4^- , FeCl_4^- , SnCl_6^- , BiCl_5^- , etc.

[0021]**[COMPOUND 3]**

Formula a

Formula b

Formula c

Formula d

[0022]**[COMPOUND 4]**

Formula e

Formula f

Formula g

Formula h

Formula i

Formula j

[0023]**[COMPOUND 5]**

Formula k

Formula l

Formula m

Formula n

Formula o

[0024]

In the cationic photopolymerization initiator (B) which has such a cation part and an anion part, a p- chlorobenzene diazonium * hexafluoro phosphate, a p- methoxybenzene diazonium * hexafluoro phosphate, a diphenyl iodonium * hexafluoro phosphate, Triphenyl sulfonium * hexafluoro phosphate, 4,4- bis- {di- (beta) (- hydroxy ethoxy) phenyl sulphonio } Phenyl sulphide-bis--hexafluoro

antimonate, 4,4- bis--{di- (beta) (- hydroxy ethoxy) phenyl sulphonio } Phenyl sulphide-bis--hexafluoro phosphate etc. is mentioned.

[0025]

Moreover, as commercial goods of a cationic photopolymerization initiator, ULTRASET of an aromatic diazonium salt (made in Asahi Denka Kogyo K.K.), AMERICUR (made in American company) etc., UVI series of an aromatic iodonium salt (made in GE company), FC series (made in 3 M company) etc., OPTOMER SP-150 of an aromatic sulfonium salt, SP-170 (made in Asahi Denka Kogyo), UVI series (made in UCC company), UVE series (made in GE company), FC series, FX series (made in 3 M company), etc., IRUGACURE 261 (made in a CIBA-GEIGY company) of a metallocene compound etc. is mentioned.

[0026]

In addition, if a photoresist and a preservation stability are considered, an aromatic sulfonium salt will be most effectively utilised as a cationic photopolymerization initiator (B).

[0027]

The effective wavelength in a dissolution of these cationic light polymerisation initiators mainly changes depending on the chemical structure of a cation. Because a cure rate mainly changes according to the variety of anion, and the variety of epoxy resin which hardens, it should just choose a suitable thing by the application.

[0028]-

In alkoxy silyl-compound (C) used with this invention, it has in a molecule the alkoxy silyl group of the at least one. It is the compound which does not have an amino group.

[0029]

Alkoxy silyl-compound (C) improves the photoresist of a photoresist composition largely. However, the alkoxy silyl compound which has an amino group is excluded from alkoxy silyl-compound (C) used with this invention, in order that the basicity of an amino group may inhibit cationic polymerisation.

[0030]

Specifically as alkoxy silyl-compound (C) used with this invention, a trimethyl methoxy silane, a trimethyl ethoxysilane, a dimethyl dimethoxysilane, a dimethyl diethoxy silane, a methyl trimethoxy silane, a tetra methoxy silane, a methyl triethoxy silane, a tetra ethoxysilane, a methyl dimethoxysilane, a methyl diethoxy silane, a dimethyl ethoxysilane, a dimethyl vinyl methoxy silane, a dimethyl vinyl ethoxysilane, a methyl vinyl dimethoxysilane, a methyl vinyl diethoxy silane, a diphenyl dimethoxysilane, phenyl trimethoxy silane, A diphenyl diethoxy silane, phenyl triethoxy silane, a vinyl triethoxy silane, 3-trimethoxy silyl propyl chloride, (gamma)-chloro propylmethyl dimethoxysilane, (gamma)-chloro propylmethyl diethoxy silane, (gamma)-mercapto propyl trimethoxy silane, (gamma) - glycidoxy propyl trimethoxy silane, (gamma)-glycidoxy propylmethyl dimethoxysilane, (gamma)-methacryloxy propyl trimethoxy silane, (gamma)-methacryloxy propylmethyl dimethoxysilane, (beta)-(3, 4-epoxy cyclohexyl) ethyl trimethoxy silane, etc. are mentioned.

[0031]

The essential component of the photoresist composition of this invention is as above-mentioned. Each is independent, or 2 or more sorts can be blended and it can be used.

[0032]

Next, the content proportion of the essential component of this invention is described.

0.1-10 weight-part content of the cationic light polymerisation initiator (B) is performed to epoxy-compound (A) 100 weight parts.

If it is less than 0.1 weight parts, the hardening (polymerisation) of the epoxy compound (A) cannot be performed sufficiently. On the one side, because an effect is saturated by 10 weight parts, even when it performs more addition, a cure rate does not rise.

[0033]

0.1-10 weight-part content of alkoxy silyl-compound (C) is performed to epoxy-compound (A) 100 weight parts.

If it is less than 0.1 weight parts, there is no hardening promotion effect, and

because an effect is saturated by 10 weight parts, even when it performs more addition on the one side, a cure rate does not rise.

[0034]

The photoresist composition of this invention contains the above-mentioned component.

However, photosensitization support agents, such as others, 2-chlorine thio xanthone, 2, 4-diiso propylthio xanthone, 2, 4-dimethyl thio xanthone, and benzophenone, Photosensitization accelerating agents, such as a triethylamine, a triethanolamine, 2-dimethylamino ethanol, a triphenylphosphine, and (beta)-thiodiglycol, Cationic thermal-polymerisation initiators, such as boron trifluoride and sulfonium ion system compounds, such as CP-66 (made in Asahi Denka Kogyo) Furthermore, making a filler, a thickener, a plasticizer, a stabilizer, a tackifier, etc. contain does not interfere.

Moreover, a small amount of solvent may be made to contain depending on necessity.

[0035]

The photoresist composition of this invention is obtained by stirring by measuring that ingredient and blending.

And, it preserves in a dark place.

[0036]

A mercury lamp, a xenon lamp, a carbon arc, a metal halide lamp, a solar light, etc. are used for the hardening of the resin composition of this invention as a source of a ultraviolet irradiation. A light ray with an including a 150-450 nm ultraviolet strength of 1-100 mW/cm-squared, What is sufficient is just to irradiate in air or inert-gas atmosphere.

When irradiating in air, as a source of irradiation, a high voltage mercury lamp is desirable.

[0037]

Moreover, to the hardening of the resin composition of this invention, the electron beam is also useable.

Especially limitation does not have an applicable electron-beam generation source, and each well-known electron-beam generator can apply.

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However, as an example, electron-beam generators, such as the Cockcroft type, the Cockcroft-Walton type, a Van de Graff type, a resonance transformer type, a transformer type, an insulated core transformer type, a DINA Mitron type, a linear filament type, and a high-frequency type, are mentioned.

In addition, the electron-beam irradiation amount in the case of a hardening changes with quantity (thickness) of a resin composition.

However, in general, it is about 0.5-30 MW in dose.

[0038]

The photoresist composition of this invention may be used as an adhesive agent or a coating agent to various material.

[0039]

[Example]

This invention is concretely explained based on an example.

[0040]

(Example)

The photoresist composition which shows a composition in Table 1 was prepared.

About these, the photoresist and the adhesive property were tested and evaluated by the following method.

The result was shown in Table 1.

[0041]

(1) As shown in the test-method diagram 1 of a photoresist, the ultraviolet of 5 mW/cm-squared strength was irradiated 20 minutes to about 3 mg sample (photoresist composition) using the photochemical-reaction calorimeter (PDSC). And, a time (T) and a heating value (DELTA) (H) until a hardening heat generation reaches a peak were measured (diagram 2 reference).

[0042]

(2) It performed based on adhesive test (cross-cut adhesion test) method JIS K 5400.

That is, a photoresist composition is coated by 50 micrometer thickness to the pane of glass degreased by the triclene.

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A ultraviolet is irradiated from 10 cm distance by the metal halide lamp (500 mJ/cm²).

Resin was made to harden.

Next, a cutter is used the centre of this resin curing substance. It cut so that every 11 perpendicular to vertical and horizontal parallel lines might be located in a line at intervals of 1 mm so that 100 measures could be done in 1 cm-squared. The cellophane tape was affixed on this resin curing substance, it removed, and the number of the measures which did not separate evaluated.

[0043]

Each example of invention is excellent in both photoresist and adhesive property clearly from Table 1.

On the one side, it is a bisphenol A type epoxy as an epoxy compound (A).

Only resin is used.

And, although Comparative Example 1 which does not include alkoxy silyl-compound (C) is excellent in an adhesive property, it is inferior to a photoresist.

Comparative Example 2 and 3 for which the cycloaliphatic epoxy resin is used as an epoxy compound (A) is excellent in a photoresist.

However, it is inferior to an adhesive property.

[0044]

[Table 1]

Table 1

Composition (weight part)

Epoxy compound (A)

Cationic light polymerisation initiator (B)

Alkoxy-silyl compound (C)

Methyl trimethoxy silane

3-trimethoxy silyl propyl chloride

Test result

A test of a photoresist

An adhesive test

A part for T

The example 1 of invention

The example 2 of invention

The example 3 of invention

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The example 4 of invention

The example 5 of invention

The example 6 of invention

The example 7 of invention

The example 8 of invention

Comparative Example 1

Comparative Example 2

Comparative Example 3

[0045]

(Explanation of the component in Table 1)

*1 A bisphenol A type epoxy resin (weight-per-epoxy-equivalent =180-200), made in Asahi Denka Kogyo K.K.

*2 A vinyl cyclohexene di oxide (weight-per-epoxy-equivalent =70-74), made in Asahi Denka Kogyo

*3 4,4- bis-{di- (beta) (- hydroxy ethoxy) Phenyl sulphonio } Phenyl sulphide-bis--hexafluoro acytemonate, made in Asahi Denka Kogyo

*4 (beta) - (3, 4-epoxy cyclohexyl) ethyl trimethoxy silane, the product made from Japanese Unika Co., Ltd.

*5 (gamma) - glycidoxy propyl trimethoxy silane, the product made from Japanese Unika Co., Ltd.

*6 (gamma) - methacryloxy propyl trimethoxy silane, the product made from Japanese Unika Co., Ltd.

[0046]

[EFFECT OF THE INVENTION]

By this-invention, the photoresist composition which is excellent in a photoresist and an adhesive property is offered.

The resin composition of this invention is hardened by irradiation of a ultraviolet and an electron beam.

However, the cure time is short.

Moreover, it has the advantage that the hardening in low temperature is possible.

Therefore, it can be used for applications, such as an adhesive agent and a coating agent.

Furthermore, with small amount, even when that characteristic does not need a

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solvent or needs the resin composition of this invention at the time of being used as an adhesive agent, a coating agent, etc., since it is sufficient, it is saving resources.

And, the environmental pollution can be prevented.

[BRIEF EXPLANATION OF DRAWINGS]

[FIGURE 1]

It is the diagram showing the test method of a photoresist on a schematic manner.

[FIGURE 2]

It is a graph explaining the test of a photoresist.

[FIGURE 1]

Ultraviolet 5 mW/cm-squared

Aluminium pan

Sensor

Sample About 3 mg

[FIGURE 2]

UV-irradiation time (minutes)

A time (minutes) until a hardening reaches a peak

Heating value (mJ/mg)

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